有機パラジウム錯体の構造、物性、触媒作用に関する計算化学的研究

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論文内容要旨

Organopalladium complexes are among the most versatile and efficient catalysts in organic synthesis as well as in several other fields of chemistry, in both laboratory-scale and industry-scale. There exist many important industrial processes catalyzed by palladium complexes and efforts are still invested to develop new ones. To improve existing catalytic processes and to develop new ones, detailed reaction mechanism analysis and characterization are significant issues. In this study, geometrical structures, properties, and details of the reaction mechanisms for processes catalyzed by organopalladium are investigated using density functional theory (DFT) method. Importance of cationic intermediate species, agostic interaction and the effect of solvent are emphasized. Discrete solvent coordinated molecules together with continuum solvent model are applied in the calculations. An original hybrid quantum chemical and classical molecular dynamics "Hybrid-Colors" is used to investigate the reaction dynamics of organometallic complex systems for the first time.

Chapter 1: Introduction

This chapter gives a brief introductory description of organometallics and homogeneous catalysis since organometallics have lots of applications to catalytic processes. General introduction on organopalladium complexes, i.e. palladium metal complexes, are also described because they are widely recognized to be the most efficient and versatile catalysts in organic synthesis. For the improvement of catalytic processes which needed detailed knowledge of catalytic system, characterization techniques for understanding structure-activity relationships are required: the importance of computational methods is also described in this chapter.

Chapter 2: Computational methods

In this chapter, the basic concepts and theoretical background of different computational techniques used in this thesis are explained. First DFT method together with the COSMO method for considering solvation effects in quantum chemical calculations is described. A hybrid quantum chemical/classical molecular dynamics method

used in Chapter 6 and theories in Colors program used for quantum chemical calculations in Hybrid-Colors program are also described.

Chapter 3: DFT studies on organo-hydride complexes of group VIII transition metal, including related complex

In this chapter, hydrido-palladium complexes are particularly studied by the use of computational methodologies. The results of DFT method investigation on geometries, electronic structures and physical properties of group VIII transition metal hydrido-Pd complexes, hydrido-Ni complexes and related complexes are discussed in this chapter. It is shown that the calculated geometries of bis-(tertiaryphosphine)hydrido-Ni and Pd complexes are in good agreement with X-ray analyzed experimental data. All structures studied have shown slightly distorted square planar conformations. Bond distances of Pd-X were elongated by changing substituents X from Cl to Br and I. The energy trend evolution and the HOMO-LUMO energy gaps for trans-$(Me_3P)_2Pd(H)X$ and trans-$(Me_3P)_2Pd(Et)X$ were shown to be Cl<Br<I.

Chapter 4: Olefin formation from ethyl-palladium complexes

In this chapter, reaction mechanisms for olefin productions from alkyl-palladium complexes, the bis-(trimethylphosphine)(ethyl)palladium(II), are analyzed by using DFT method. The previously published experimental results reported the reaction pathway of the olefin formation proceeded mostly via cationic palladium(II) complex intermediates. To compare reaction mechanisms involving cationic Pd^{II} complex intermediates with those involving neutral Pd^{II} complex intermediates, a calculation model with discrete solvent molecules on the central Pd^{II} complex has been proposed and to include solvent screening effects, COSMO method has been used. Using this methodology, decomposition of a series of monoethyl-palladium(II) complexes having electronegative ligands, $Et\text{-}Pd^{II}(PMe_3)_2(X)\cdot S_2$, where X = Cl, Br, I, and S = Acetonitrile, to produce olefin and hydrido-Pd^{II} complex have been examined. In the β-hydrogen elimination process, an agostic Pd^{II} complex intermediate plays an important role. A cationic agostic Pd^{II} complex is well stabilized and is obtained at an equilibrium state of a low energy level. Removal of an electronegative ligand of a Pd^{II} complex by $AgBF_4$ forms a cationic Pd^{II} species and the cationic agostic Pd^{II} complex having BF_4^- as a counter anion shows the relative energy at much lower level. A new calculation methodology to include solvent effects, to investigate the reaction mechanisms of olefin production from alkyl-Pd^{II} complexes via cationic Pd^{II} complex species has been developed successfully. The results reveal that following the neutral species pathway, agostic intermediates cannot be stabilized, whereas following the cationic species pathway, agostic intermediates are obtained as local equilibrium states, taking critical roles in the reaction course. Relative energy levels of agostic Pd complexes change as follows with variation of the counter anion: Cl > Br > I >> BF_4. The model used in this chapter can be used to evaluate reaction intermediates, including both counter anion effects, and solvent effects.

Chapter 5: Homogeneous catalysis system: Heck reaction mechanism

In this chapter theoretical investigation on reaction mechanisms for the Heck olefin arylation catalyzed by palladium complex was explored. From this study, it has been revealed that cationic catalyst species play an important role in the process of olefin production from alkyl-palladium(II) complexes, where cationic catalyst species were stabilized with solvent effects. In order to investigate the involvement of a cationic catalyst species in the Heck reaction cycle, a model with two discrete solvent molecules was adopted. To stabilize cationic Pd^{II} species, COSMO method was applied. Using these new calculation methodologies, Heck reaction mechanisms involving cationic Pd^{II} species were studied successfully. The cationic agostic Pd^{II} complex, the important intermediate in the olefin production, was found to be stabilized at fairly low energy level and was obtained as the equilibrium state. The new reaction pathway involving the cationic palladium species was found to be more feasible than the reaction pathway involving Pd(0) complex. Direct pathway without taking Pd(0) complex state is feasible, where cationic bis(trimethylphosphine)hydrido-Pd(II) bromide complex reacts with phenyl bromide in the presence of a base to produce cationic bis-(trimethylphosphine)phenyl-Pd(II)bromide complex.

Chapter 6: Application of hybrid classical and quantum chemical molecular dynamics for investigating the dynamic behavior of hydrogenation of carboxylic anhydride catalyzed by palladium complex

In this chapter the hydrogenation of carboxylic acid anhydride catalyzed by Pd complexes is studied using a novel hybrid quantum chemical/classical molecular dynamics "Hybrid-Colors" program. In order to realize high accuracy comparable to the first-principles calculation, parameters for Colors program, which is used for quantum chemical calculation in Hybrid-Colors program, were determined on the basis of DFT method employing Amsterdam Density Functional program (ADF). The determined parameters were applied to several molecules as well as to investigate the dynamics of reaction. Good agreement for the geometries, atomic charges and binding energies were obtained by ADF and Colors. Furthermore, the validity of the parameters in the quantum chemical molecular dynamics simulation has been verified. Electronic states and reaction dynamics were analyzed employing large model of palladium catalysts. It is shown that acetaldehyde and acetic acid are produced successfully, and the catalysts are regenerated at the end of the simulation, reproducing the experimental and the DFT calculation results. The bond population analyses were also shown to confirm these results.

Chapter 7: Summary

This chapter gives a summary of the results in the previous chapters and the main conclusions of this thesis. This can be briefly mentioned as follows: (i) theoretical investigations with both DFT and hybrid quantum chemical/classical molecular dynamics were performed on the organopalladium complexes, mainly geometrical structures, properties and details of the reaction mechanisms catalyzed by organopalladium were investigated by the use of DFT method, whereas a hybrid quantum chemical and classical molecular dynamics "Hybrid-Colors" has been used to investigate reaction dynamics of an organometallic for the first time. (ii) Geometries of hydrido-Pd and Ni complexes obtained by DFT calculations have shown a good agreement with experimental

X-ray data. (iii) The thesis gives a new insight to evaluate reaction intermediates, including counter anion and solvent effects. The COSMO method with discrete solvent molecules coordinated to the central Pd atom of the complex was successfully applied and it was clarified that the solvent lowers the energy levels of intermediates. (iv) In the production of olefins from alkyl-Pd-complexes, models for calculating solvated cationic palladium complexes together with counter anions were explored and suggested: the reaction pathway following the cationic species is preferable as compared to that following the neutral species pathway, the cationic agostic intermediates are obtained as local equilibrium states and it is observed that they play an important role in the reaction course which is to lower relative energies. The relative energy levels for cationic agostic are decreased by changing counter anion: Cl>Br>I>>BF_4. (v) New reaction mechanism involving cationic organopaladium complex is proposed for Heck olefin arylation reaction. Direct pathway without taking Pd(0) complex state is feasible, that is the cationic bis-(trimethylphoshine)phenylPd(II) bromide reacting with phenyl-bromide in the presence of a base to form the cationic bis-(trimethylphosphine)phenylPd(II) bromide complex. (vi) Reliable and much faster program "Hybrid-Colors" has been applied successfully to investigate the dynamics of reaction systems catalyzed by organo-palladium complexes for the first time. Results are consistent with those by DFT method, and also agree well with the previous experimental reports.

In this thesis, not only information about structures and properties of compounds were obtained but also the challenge of studying elusive reaction mechanisms at the atomistic level, considering intricate solvent effects, especially, those involved in homogeneous catalysis of organopalladium. The practically usefulness of these studies are evident since they will constitute a cornerstone in investigations leading to more versatile and efficient organopalladium catalysts in the world of science in general and chemistry in particular.

論文審査結果の要旨

有機パラジウム錯体は有機合成において最も効率的な触媒の一つであり、様々な産業分野において用いられている。有機パラジウム錯体による触媒プロセスのさらなる高効率化のために、反応機構の解明に向けた数多くの研究がなされている。本研究では、有機パラジウム錯体の構造、物性、触媒作用について密度汎関数法を用いて解析し、カチオン中間体の重要性、反応中における相互作用、溶媒の効果について解明した。特に溶媒の効果については連続体溶媒モデル及び溶媒分子を顕に考慮したモデルによりその差異を明確に示すことに成功した。また、ハイブリッド Tight-Binding 量子分子動力学法により有機金属錯体の反応ダイナミクスの理論的解明に初めて成功した。

本論文は「Computational Chemistry Studies on Organopalladium Complexes: Structures, Properties and Catalysis (有機パラジウム錯体の構造、物性、触媒作用に関する計算化学的研究)」と題し、7 章から成る。

第 1 章は緒言である。有機金属錯体や均一系触媒について概説し、産業上特に重要な有機パラジウム錯体について詳細に説明した。触媒プロセス効率化のための反応機構解明の重要性について述べ、本論文の目的を明確にするとともに、反応機構解明の手法として計算化学手法の重要性について強調している。

第 2 章においては、本論文において用いた計算化学手法について説明している。最初に密度汎関数法及び量子化学計算において溶媒の分極の効果を取り扱うための COSMO 法について説明し、続いて、反応中心に量子化学計算を適用し周辺は古典論的に取り扱うことで大規模系の反応ダイナミクスを実現可能な新規手法ハイブリッド Tight-Binding 量子分子動力学法について説明している。

第 3 章においては、8 族の遷移金属の水素化有機錯体について密度汎関数法を用いて解析している。密度汎関数法により Pd や Ni などをはじめとする錯体系について構造、電子状態、物性について計算した。得られた結果は実験による X 線解析の結果を再現することに成功している。また、パラジウムに配位する陰イオンの結合距離の序列について解明している。

第 4 章においては、アルキルパラジウム錯体からのオレフィン生成機構について密度汎関数法を用いて解析している。実験的に言われているカチオン Pd(II)を介する反応経路と中性 Pd を介する反応経路についてエネルギー的に評価した。Pd 錯体に直接配位する溶媒分子については顕に取り扱い、その他の溶媒は連続体モデルを用いて計算を行うことにより、反応中間体、反応経路、カウンター陰イオン及び溶媒の効果を解明することに成功している。

第 5 章においては、パラジウム錯体によるヘックオレフィンアリル化反応機構について密度汎関数法を用いて解析している。カチオン中間体と中性中間体を経由する反応経路の比較からアルキルパラジウムからのオレフィン生成においてカチオン触媒種が重要な役割を担っていることを示すとともに、前章同様のモデルを用いて溶媒の効果をも解明している。

第 6 章においては、有機パラジウム錯体によるカルボン酸無水物の水素化反応に、新規手法であるハイブリッド量子分子動力学法を応用し、反応ダイナミクスの解明に初めて成功している。ハイブリッド Tight-Binding 量子分子動力学法における量子計算に用いられる Tight-Binding 量子分子動力学法のためのパラメータの妥当性を検証した後に有機パラジウム錯体によるカルボン酸無水物の水素化反応ダイナミクスへと同手法を応用し、反応ダイナミクスの解明に成功している。

第 7 章は本論文のまとめである。

以上要するに、本論文は計算化学手法により有機パラジウム錯体の構造、物性、触媒作用について解明することに成功しており、理論的に反応機構を解明する手法を確立している。得られた成果は産業分野において活用されている有機 Pd 錯体触媒の高効率化のための知見を与えるものであり、その意義は大きい。

よって、本論文は博士(工学)の学位論文として合格と認める。